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Synthesis and self-organization of PPV-based block copolymers for photonic applications

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Abstract

Rod–coil block copolymers have been synthesized with the objective of enhancing the photovoltaic efficiency by the incorporation of both donor and acceptor components in a molecular architecture that is self-structuring. Block copolymers were obtained by using an end-functionalized rigid-rod block of poly(2,5-dioctyloxy-1,4-phenylenevinylene) (PPV) as a macroinitiator for the nitroxide-mediated controlled radical polymerization of a flexible, styrene-based block. Under suitable conditions the formation of honeycomb structures by PPV-*block*-polystyrene (PPV-*b*-PS) is observed. The honeycomb structure consists of a 2-dimensional array of spherical air holes with an inner diameter of 3 – 5 μm in a polymeric film, which results in ~ 6.5 million hexagonally packed holes per square centimeter. The application of these structures as templates for highly ordered functional patterns is demonstrated by evaporating aluminum on this regularly structured surface and subsequently washing away the polymer.

Keywords: Semiconducting films, Structural phase transitions, Poly(phenylene vinylene) and derivatives, Fullerenes and derivatives, Solar cells

1. Introduction

For the last decade, research on photonic devices, such as Light-Emitting Diodes (LED) or photovoltaic (PV) cells, using organic materials has received increasing attention and shows steady improvement of performances [1]. Very often, poly(*p*-phenylene vinylene) (PPV) derivatives are used in such devices [1]. In the case of PV cells, PPV can act as donor, but not readily as acceptor for electrons. To circumvent this, devices based on mixtures of several materials. Blending, however, can lead to phase separation of the different components on a macroscopic scale. Since the interface between the different components is the active area for the essential process of electron transfer, an increase of the interfacial area should lead to enhanced performance [2]. Thus, phase separation on a nanometer scale should be favorable. This last feature is well known for block copolymers as microphase separation. Our approach to improve device performance is to synthesize donor–acceptor diblock copolymers, thereby promoting the ordered self-structuring of the functional components.

With photovoltaic cells as the target application, the block copolymers consist of a PPV (rigid rod) block and a styrene (coil) block that is subsequently functionalized with fullerene molecules. The best method to control the synthesis of block copolymers utilizes living polymerization techniques. Thus, we developed a new synthetic strategy to obtain the target systems. Since radical polymerizations tolerate a wide variety of functional groups, they offer the opportunity to use such sensitive materials as PPV as a macroinitiator.

Lately it was observed that rod–coil block copolymers, when thin films are cast from appropriate solvents on solid substrates, spontaneously form highly ordered, micro-porous honeycomb structures with a characteristic length scale of a few micrometers [3–5]. The porous character and the increased surface area obtained through the pattern formation could be advantageous for the use of the block copolymer in photovoltaic cells, reducing the reflection of light.

Recently we demonstrated not only the synthesis of PPV-based block copolymers by using the nitroxide-mediated radical polymerization technique, but also the functionalization of these rod–coil block copolymers with C_{60}, thereby creating donor–acceptor block copolymers [6]. Here, we demonstrate the formation of honeycomb structures by this type of block copolymers and the use of the highly ordered, micro-porous films as a template for creating patterned aluminium structures.

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2. Experimental

The synthesis and characterization of the macroinitiator and the block copolymers are described elsewere [6]. The general structure of the block copolymers is shown in Fig. 1.

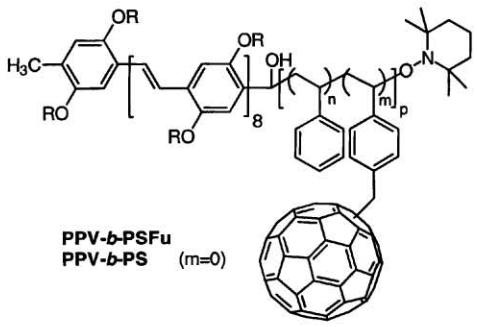

Fig. 1. Structure of block copolymers used for photonic applications

By drop-casting a CS_2 solution of the PPV-*b*-PS block copolymer on solid substrates in a flow-hood, we obtained the honeycomb structures (Fig. 2A, 2B). The processing steps in creating a regular pattern of aluminum are as follows. First, the honeycomb structure was exposed to blue light (475 – 495 nm) for 10 min, whereby only the exposed surface of the polymer matrix is photo-crosslinked. Subsequently, a 40 nm layer of aluminum was vapor-deposited onto the polymeric honeycomb structure. After removing the aluminum-coated top layer with Scotch™-tape and washing away the unexposed polymer layer with chloroform, a hexagonally packed array of aluminum cups remains on the surface (Fig. 2C, 2D) [7].

3. Results and discussion

By preparing films from CS_2 solution, patterned films consisting of a hexagonal array of air holes in a polymer matrix, as shown in Fig. 2A and 2B, can be obtained under suitable conditions [7]. The same patterns can also be obtained with PPV-*b*-PSFu. Fluorescence microscopy images of films of the latter had to be recorded with exposure times 3 orders of magnitude longer than for PPV-*b*-PS, indicating effective luminescence quenching by the fullerene moieties. The porous character and the increased surface area obtained through the pattern formation could be advantageous for the use of the block copolymer in photovoltaic cells, reducing the reflection of light.

The open character of the honeycomb films were successfully used as templates for highly-ordered functional dots. As the polymer film must be washed away after the deposition process, one is restricted to materials that are insoluble in the polymer solvent, e.g. aluminum. The aluminum cups are bowl-like disks with a diameter of 3.5 μm and a height of 200 nm at the edges and 40 nm in the center of the cups. The shape of the cups is obviously due to the spherical shape of the cavities in the honeycomb structure. The process results in roughly 6.5×10^6 cups of aluminum per square centimeter [7]. Since all fluorescent material had been washed away, a fluorescence microscopy image could not be obtained (Fig. 2D).

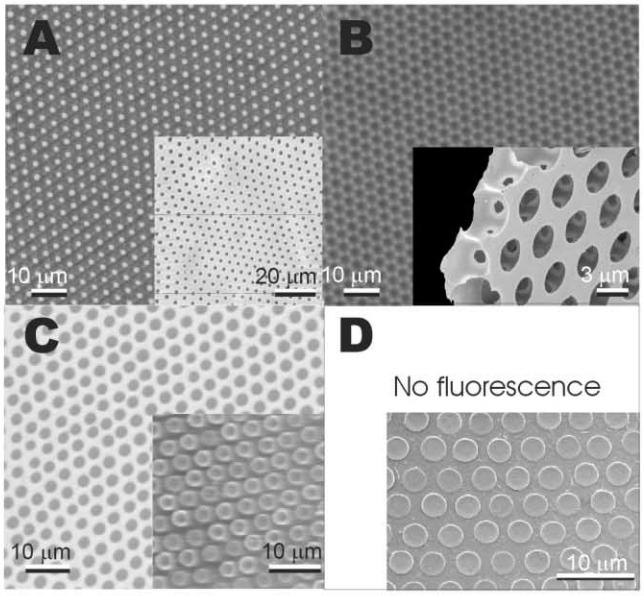

Fig. 2. Honeycomb pattern of PPV-*b*-PS as imaged with A) optical microscopy and AFM (inset) and B) fluorescence microscopy and SEM (inset). Patterned aluminum dots as imaged with C) optical microscopy and AFM (inset) and D) fluorescence microscopy and SEM (inset).

4. Conclusions

Rod–coil and donor–acceptor block copolymers were used to obtain honeycomb structured films upon casting films from CS_2 solution under suitable conditions. These micro-porous films can be used as templates for highly-ordered functional patterns e.g. of aluminum cups.

5. Acknowledgment

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